I. THE REACTIONS OF 2-PHENYL-BENZISOSULFONAZOLE

II. THE STRUCTURE OF THE BISULFITE COMPOUND OF ACETALDEHYDE

BY

ANTHONY HAMILTON LAND

B.S., University of Kentucky, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. THE REACTIONS OF 2-PHENYLBENZISOSULFONAZOLE

INTRODUCTION

2-Phenylbenzisosulfonazole is a member of a group of compounds known as sultims which are derived by intramolecular dehydration from aromatic sulfonamides having a carbonyl group in the ortho position. Although several such compounds have been prepared, little is known of their chemical behavior.

Attention was drawn to the above mentioned sultim by the observation of its hitherto unreported property of dissolving in caustic alkali and being reprecipitated in its original form by subsequent acidification.[1]

The present investigation was undertaken in order to arrive at an explanation of this phenomenon and to study the chemical behavior of this compound toward certain other reagents.

DISCUSSION OF RESULTS

Since the sultim structure *per se* has no acidic hydrogen atom, its behavior toward alkali must be the result of a readily reversible hydrolytic cleavage which gives rise to a weakly acidic compound. Depending upon the manner in which the hydrolysis takes place, this acidic compound may be either 1,2-dihydro-2-phenylbenzisosulfonazolol-2 or *o*-benzoylbenzenesulfonamide.

The salt was formed only in the presence of a substantial excess of caustic alkali and could not be isolated in the pure state.

Methylation of the salt in the presence of an excess of sodium hydroxide yielded *N,N*-dimethyl-*o*-benzoylbenzenesulfonamide, indicating that the salt possessed the acyclic structure. On the other hand, the formation of the cyclic 1,2-dihydro-2-phenylbenzisosulfonazole-2-carboxylic acid by the addition of sodium cyanide to the sultim followed by hydrolysis of the resulting nitrile favored the cyclic structure for the salt. These apparently conflicting results indicate that the salt is a tautomeric mixture of the cyclic and acyclic structures.

The sultim has been reported to yield benzohydrol-*o* sulfonic acid when reduced with zinc and sodium hydroxide in a water-alcohol solution.[1] A similar reduction in either alcoholic sodium hydroxide or glacial acetic-hydrochloric acid solution was found to yield 1,2-dihydro-2-phenylbenzisosulfonazole.

Grignard reagents added to the carbon-nitrogen double bond of the sultim, producing 2-alkyl or 2-aryl-1,2-dihydro-2-phenylbenzisosulfonazoles.

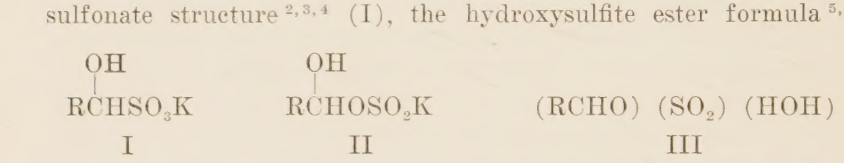
SUMMARY

A study of the sultim, 2-phenylbenzisosulfonazole has been carried out. It was found that: (a) methyl sulfate and alkali converted it into *N*,*N*-dimethyl-*o*-benzoylbenzenesulfonamide; (b) zinc and hydrochloric acid reduced it to 1,2-dihydro-2-phenylbenzisosulfonazole; (c) treatment with sodium cyanide followed by hydrolysis produced 1,2-dihydro-2-phenylbenzisosulfonazole-2-carboxylic acid; (d) phenyl- and ethylmagnesium bromides added to the carbon-nitrogen double bond, producing 1,2-dihydro-2,2-diphenylbenzisosulfonazole and 1,2-dihydro-2-ethyl-2-phenylbenzisosulfonazole respectively.

II. THE STRUCTURE OF THE BISULFITE COMPOUND OF ACETALDEHYDE

INTRODUCTION

The structure of the compounds resulting from the addition of alkali metal bisulfites to aldehydes and certain ketones has been the subject of much discussion and experimentation. Various investigators have, from time to time, favored either the hydroxysulfonate structure [2,3,4] (I), the hydroxysulfite ester formula [5,6]



I II III

(II), or a "polymolecule" formula [7,8] (III). The experiments of Raschig and Prahl,[4,9] Backer and Mulder,[10] and the recent work of Lauer and Langkammer [11] leave no doubt that the bisulfite compound of formaldehyde is best represented by the hydroxysulfonate structure (I). By inference, other bisulfite compounds should possess the same structure. However, in view of the occasional exceptional behavior of formaldehyde as compared to other aldehydes, it was desirable to investigate the structure of the acetaldehyde bisulfite compound in order to add further evidence on the structure of these compounds.

EXPERIMENTAL

α-Chloroethanesulfonamide was prepared and observed to be readily decomposed into acetaldehyde when boiled with a dilute solution of potassium hydroxide. This reaction was presumed to involve the intermediate formation of α-hydroxyethanesulfonamide

from which acetaldehyde was produced by hydrolytic cleavage of the weakened carbon-sulfur bond. Under similar conditions the chlorine atom of potassium α-chloroethanesulfonate was not replaced by a hydroxyl group and no acetaldehyde was produced.

Acetaldehyde-sodium bisulfite was transformed into α-aminoethanesulfonic acid by treatment with aqueous ammonia and subsequent acidification.[12] This compound was converted into α-chloroethanesulfonic acid by reaction with nitrosyl chloride in the presence of concentrated hydrochloric acid at 0°. The potassium salt of this acid reacted with phosphorus pentachloride, yielding α-chloroethanesulfonyl chloride which was converted to the corresponding sulfonamide by the action of dry ammonia.

α-Chloroethanesulfonyl chloride was prepared by chlorination of a water suspension of trithioacetaldehyde.[13] A portion of the acid chloride thus obtained was converted by hydrolysis with barium hydroxide into barium α-chloroethanesulfonate from which the corresponding potassium salt was obtained by metathesis with potassium sulfate. A second portion of the acid chloride was converted to the amide as described above. Both the potassium salt and the amide thus obtained were identical with those prepared from acetaldehyde-bisulfite, demonstrating the presence of a carbon to sulfur linkage in the latter.

Acetaldehyde-potassium bisulfite reacted with acetic anhydride in pyridine, producing potassium α-acetoxyethanesulfonate which was relatively stable toward acids and alkalis but was readily converted into α-acetoxypropinitrile by an aqueous solution of sodium cyanide.

SUMMARY

A study has been made of some derivatives of α-chloroethanesulfonic acid. Its potassium salt was found to be resistant to alkaline hydrolysis but the amide was readily converted into acetaldehyde by heating with dilute alkali.

The presence of a carbon to sulfur linkage in potassium acetaldehyde bisulfite has been demonstrated by its conversion through α-aminoethanesulfonic acid, potassium α-chloroethanesulfonate, and α-chloroethanesulfonylchloride to α-chloroethanesulfonamide.

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VITA

The writer was born in Lexington, Kentucky, on January 15, 1914. He attended the public schools of Lexington and was granted the degree of Bachelor of Science by the University of Kentucky in June, 1936. He was an assistant in chemistry during a year of graduate study at that institution. He entered the Graduate School of the University of Illinois in September, 1937, and held a teaching assistantship in analytical chemistry from 1938-1941.

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